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Photoacoustic spectroscopy and characterization of some high temperature superconducting oxide (HITSO) materials

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Abstract : This review article attempts to explore, possibly for the first time, the enormous possibilities of using a non-destructive photoacoustic spectroscopic (PAS) technique for the characterizations of high temperature superconducting oxide (HITSO) materials. The thermal variations of the photoacoustic amplitude and phases of different HITSO materials have been analysed on the basis of the Rosencwaig-Gersho (R-G) model. From these experimental data the thermal diffusivity of the superconducting materials like Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O have also been calculated. These studies provide interesting information about the importance of electron-phonon, and phonon-phonon interactions to elucidate the mechanism of high temperature superconductivity in these oxide materials. Based on the information, we also put forward a simple mechanism for high T_c superconductivity in oxides. It has finally been confirmed from all these investigations that PAS might be a very important tool for the characterizations of opaque (HITSO) materials along with other solids, liquids and gases.

Keywords : Photoacoustic spectroscopy, high temperature superconductivity, thermal diffusivity.

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Plan of the Article :

1. Introduction

Photoacoustic spectroscopy (PAS) is one of the highly sophisticated techniques for the non-destructive characterizations of any kind of materials (like glasses, gels, crystalline solids,

thin films, liquids etc.). The PAS might also be compared with the tunneling microscopy when photoacoustic spectroscopy is used as PA microscope.

Though many interesting observations like phase transitions, thermal diffusivity, optical absorption etc. of different crystalline and amorphous solids have been investigated with PAS, very little investigations have so far been made on the newly discovered high temperature superconducting oxides HITSO. The aim of this review is to focus our attention to the interesting observations made so far on HITSO materials using PAS and also to draw research interest in this highly important technique where both optical and acoustical effects are being used for a non-destructive characterizations of HITSO or any other materials. Since the photoacoustic method of characterizing materials is relatively new (though PAS effect was discovered by Alexander Graham Bell more than a century ago), the potentiality of the technique remained almost unexplored until recently. With the discovery of very sensitive piezoelectric materials necessary for the PAS investigations, very recently a new trend is being visualized to focus the universality of the technique. We shall discuss first the PAS technique and the theoretical development made to understand the photoacoustic (PA) signals before we go for discussion of the PAS technique for studying HITSO materials of persent interest.

2. Photoacoustic spectroscopy (PAS)

Optical spectroscopy is a versatile tool for the enormous growth of atomic and molecular physics and also for the development of quantum mechanics. This is mainly because of the non-destructive character of the spectroscopic observation. But the great problems one has to face with usual optical spectroscopy are associated with very weak and strong light absorbing samples (or strong light scattering samples). The various techniques like derivative spectroscopy etc. have already been proved to be inadequate to deal with such problems. For opaque samples there is practically no transmitted photons causing absorption measurements very difficult, if not impossible. The method of diffuse reflectance [1], attenuated total reflection and internal reflection spectroscopy [2], and even Raman scattering spectroscopy [3] have not been very useful to study opaque and highly light scattering samples or they are useful only in a limitted frequency ranges under specific conditions.

The photoacoustic or optoacoustic spectroscopic techniques are being used for the last one and a half decade as a very powerful tool for the studies of such substances, not found suitable to investigate with other spectroscopic techniques. The HITSO materials of our present interest are also very dark and hence incovenient for usual spectroscopic studies necessary for their detailed characterizations.

2.1. The PAS technique :

The PAS technique involves in the detection of optical effect by acoustic method. When the former is absorbed by the substance the acoustic effect is generated. The acoustic singal generated due to the absorption of the incident light frequency is detected and analysed to

characterize the samples. The incident light energy excites the internal energy levels of the samples and upon subsequent de-excitation, all or part of the absorbed photon energy is converted into heat through non-radiative de-excitation process. In case of gas and liquid samples, the internal heating (due to absorption of light) caused pressure fluctuations having the same frequency as that of the modulation of the incident beam, which is detected by an acoustic transducer. In solid samples like HITSO, the periodic heating of the samples results in a periodic heat flow from the interior of the sample to the surrounding gas in the sample cell which in turn produces pressure fluctuations in the gas to be detected properly.

One may, therefore, consider the PAS as a combination of optical absorption spectroscopy and calorimetry where the heat input is supplied by the incident light and the rise of temperature is indirectly measured by acoustic method with a microphone/piezo-ceramics. During this treatment, temperature rise may be of the order of 10^{-5} to 10^{-7}°C, depending on the sample's light absorbing capacity. However, PA signal is insensitive to the non-absorbed light —one of the greatest advantages of the PAS system over many other spectroscopic techniques.

3. The basic theory for PAS

Adequate understanding of the photoacoustic effect has not yet been possible. This is mainly because of its involvement with heat capacity, thermal conductivity, optical absorption etc. parameters, characterizing the samples. However, first successful attempt to develop an exact theory of PA effect in solids was carried out by Parker [4] which was followed by the pioneering work done by Rosencwaig and Gersho [5, 6] (the R-G theory). According to this theory, the PA signal depends both on the generation of the acoustic pressure disturbance at the sample—gas interface and on the transport of this pressure distribution through the gas to the detecting microphon [7]. The pressure fluctuations at the sample-gas interface are caused by the periodic heat flow from the sample governed by thermal diffusion process described by some equation. The (R-G) theory first solved these equations for the sample, the backing materials on which the sample is mounted, and the gas in the cell, and finally obtained an exact expression for the periodic temperature fuctuation (and hence pressure fluctuation) at the sample-gas interface.

3.1. The (R-G) theory :

The (R-G) theory has been used widely for interpreting the results of the PA signals. This theory will therefore be used for the investigation of the PA signal of the HITSO materials of our present interest. For one dimensional analysis of the PA signal in a simple cylindrical cell, we consider the following Figure 1. The cell has a diameter (d), length (L) such that $L << \lambda_a$, wavelength of the acoustic signal. The intensity I of a sinusoidally modulated monochromatic beam of light (wavelength λ) is given by

$$2I = I_0 (1 + \cos \omega t) \tag{1}$$

where I_0 is the intensity of the incident light flux (W/cm^2) and ω denotes the modulated frequency. The heat density H produced at a point in the solid is

$$H = 1/2\,\beta I_0 e^{\beta x}(1 + \cos \omega t) \tag{2}$$

with optical absorption coefficient β of the solid sample for wavelength λ. The solid sample extends from $x = 0$ to $x = -L$ with light incident at $x = 0$. The thermal diffusion equation for the sample taking into account the distributed heat source due to illumination (eq. 2) can be written as

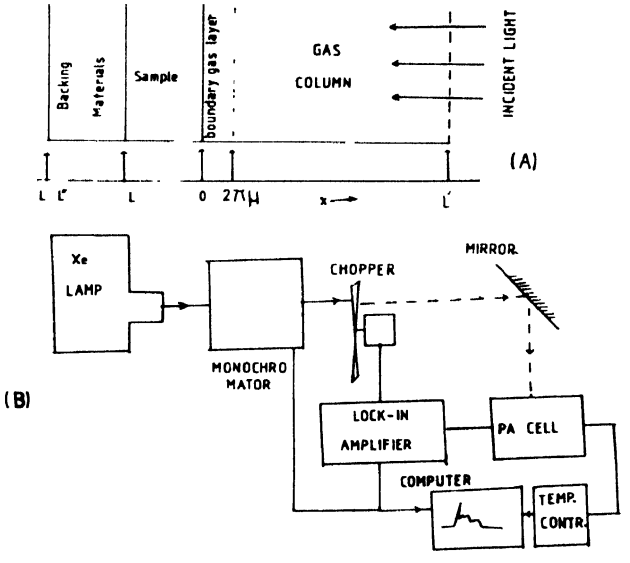

Figure 1. (a) A simple cylindrical photoacoustic cell (cross sectional view). (b) A block diagram of the photoacoustic spectrometer

$$\frac{\partial^2\theta}{\partial x^2} = \frac{1}{\alpha}\left(\frac{\partial\theta}{\partial t}\right) - Ae^{\beta x}(1 + e^{i\omega t}) \qquad \text{for} \quad -L \le x \le 0 \tag{3}$$

where $A = I_0\beta\eta/2K$ (K is the thermal conductivity of the sample) and $\alpha = K/\rho C$ (ρ = density, C = specific heat), and η is the efficiency with which the absorbed light is converted into heat through non-radiative relaxation process. A reasonable assumption for most solids is to take η as unity at room temperature. The thermal diffusion equations for the backing materials and the gas in the volume are, respectively, written as

$$\frac{\partial^2\theta}{\partial x^2} = \frac{1}{\alpha'}\left(\frac{\partial\theta}{\partial t}\right), \qquad -L'' - L \le x \le -L \tag{4}$$

$$\frac{\partial^2\theta}{\partial x^2} = \frac{1}{\alpha}\left(\frac{\partial\theta}{\partial t}\right), \qquad 0 - L \le x \le -L'' \tag{5}$$

Using appropriate boundary conditions, the solutions for $\theta(x, t)$ in the cell neglecting transients can be expressed as

$$\theta(x, t) = \begin{cases} \dfrac{1}{L''}(x + L + L'')W_0 + W e^{\sigma''}(x + L)\, e^{it} & -L - L'' \le x \le -L \\ b_1 + b_1 x + b_3 e^{\beta x} + (Ue^{-\sigma' x} Ve^{-\sigma' x} - Ee^{\beta x})\, e^{it} & -L \le x \le 0 \end{cases}$$

$$(1 - \frac{x}{L''})F + \theta_0 e^{\sigma' x} e^{i\omega t}, \qquad 0 \le x \le L \tag{6}$$

The real part of the complex valued solution of $\theta(x, t)$ is the solution of all physical interest and repesents the temperature in the cell relative to ambient, as a function of time. The parameters W, U, V, and θ_0 are complex valued constants, b_1, b_2, b_3, W_0 and F are real valued constants, and $\sigma = (1 + i)a$. Attributing suitable boundary conditions all the constants of eq. (6) and hence the real (dc) and frequency dependent (ac) components of the solution can be obtained. The complex amplitude of the periodic temperature θ_0, at the HITSO -gas boundary ($x = 0$) can be expressed as

$$\theta_0 = \frac{\beta I_0}{2K(\beta^2 - \sigma^2)} \left[\frac{(r-1)(b+1)e^{\sigma L} - (r+1)(b-1)e^{-\sigma L} + 2(b-r)e^{-\beta L}}{(g+1)(b+1)e^{\sigma L} - (g-1)(b-1)e^{-\sigma L}} \right] \tag{7}$$

with $b = Ka''/Ka$, $g = Ka'/ka$, and $r = (1 - i)\beta/2a$.

The periodic temperature variation at the surface of the sample governed by (eq. 7) gives rise to thermal waves to diffuse into the surrounding gas which in turn produces a periodic temperature variation in the gas given by the a.c. component of the solution (6)

$$\theta_{ac}(x, t) = \theta_0 e^{-\sigma' x} e^{i\omega t}. \tag{8}$$

The time dependent component of the temperature in the gas (eq. 8) attenuates rapidly to zero with increasing distance from the surface and fully damped out at a distance of $2\pi/a = 2\pi\mu'$ (μ' = thermal diffusion length of the gas). Practically a gas layer of thickness $2\pi\mu'$ is responsible for periodic temperature variation at the sample surface. The boundary layer of the gas can be thought of as acting as an acoustic piston whose displacement is given by

$$dx(t) = 2\pi\mu' \frac{\theta(t)}{T_0} = \frac{\theta_0 \mu'}{\sqrt{2}T_0} \times e^{i(\omega t - \pi/4)}. \tag{9}$$

The acoustic pressure in the cell due to this displacement of the piston can be obtained from the adiabatic gas law, viz

$$PV^{\gamma} = \text{const.}$$

where P = pressure, V = volume in the cell and γ is the ratio of specific heats of the gas. The actual pressure variation $P(t)$ is given by the real part of $P(t)$ as

$$\Delta P(t) = Q_1 \cos(\omega t - \pi/4) - Q_2 \sin(\omega t - \pi/4)$$

or
$$\Delta P(t) = q \cos(\omega t - \psi - \pi/4). \tag{10}$$

Q_1 and Q_2 are the real and imaginary parts of Q, q and ψ are the amplitude and phase of Q, that is

$$Q = Q_1 + iQ_2 = qe^{i\psi}. \tag{11}$$

Here, Q specifies the complex envelope of the sinusoidal pressure variation, and the explicit formula for Q is

$$Q = \frac{\beta I_0 \gamma P_0}{2\sqrt{2}T_0 KL'a'(\beta^2 - \sigma^2)} \quad \frac{(r-1)(b+1)e^{\sigma L} - (r+1)(b-1)e^{-\sigma L} + 2(b-r)e^{-\beta L}}{(g+1)(b+1)e^{\sigma L} - (g-1)(b-1)e^{-\sigma L}} \tag{12}$$

which gives the amplitude and phase of the acoustic pressure wave generated in the cell by photoacoustic effect.

For optically opaque solids like (HITSO) where most of the light is absorbed within a distance that is small compared to L and essentially no light is transmitted. For thermally thin solids ($\mu \gg L$; $\mu \gg L_\beta$) [$L_\beta = 1/\beta$ is the optical absorption length, μ is the thermal diffusion length and L is the sample thickness]. For all cases it is assumed that $g < b$, and $b \sim 1$. One may also conveniently write $Y = \gamma P_0 T_0 / 2\sqrt{2}T_0 L'$ appearing as constant in the expression for Q. Here one may use $e^{-\beta L} \approx 1 - \beta L$, $e^{\pm\sigma L} \approx 1$ and $|r| \gg 1$.

Therefore, $Q = \frac{(1-i)}{2a'} \left(\frac{\mu''}{R''}\right) Y.$ (13)

Thus, the acoustic signal is independent of β, but it depends on the thermal properties of the backing materials, and varies as ω^{-1}.

Again for thermally thick solids ($\mu < L$; $\mu > L_\beta$) and hence $e^{\beta L} \approx 1 - \beta L$, $e^{-\sigma L} \approx 1 - \beta L$, and $|r| \ll 1$.

Therefore, $Q = \frac{\gamma}{2a'aK\beta}(\beta - 2a - i\beta) = \frac{-i}{2a'}(\mu/K)\, Y.$ (14)

Here the sample is optically opaque, but it is not photoacoustically opaque as long as $\mu < L$. That is, the PA signal is proportional to β and depends on the thermal properties of the sample and various as $\omega^{-3/2}$.

Similarly, one may calculate the special cases with optically transparent solids ($L_\beta > L$) which is not applicable for the HITSO materials of our present interest and therefore not discussed.

The main characteristic features of the R–G theory developed so far, has been verified by several researchers [8–10]. McDonald and Wetsel [11] extended the R–G theory to include the effect of thermally induced mechanical vibration of the samples. However, inspite of these refinements, the R–G theory still remains a valid theory for studying photoacoustic properties of solids, liquids, or gases.

4. PAS for HITSO materials

Various techniques have so far been developed to characterize the high T_c superconducting materials like La–(Sr, Ba)–Cu–O, Y(Ln)–Ba–Cu–O, Bi–Sr–Ca–Cu–O, Tl–Ca–Ba–Cu–O etc. having superconducting transition temperatures in the range of 30–40K, 90–115K, 60–110K, 90–125K, respectively [Joshi *et al* 12] and for further references please see the Progress in high Temperature Superconductivity Vol. 1–21 published by World Scientific, Singapore, during 1987-1989 and also Physica (Superconductivity), 1988–1990]. All these materials are little paramagnetic before the superconducting transition (i.e. in the normal states) with square–planar Cu-coordinations.

It is well known that specific heat C_p and thermal conductivity (K) give many salient features of superconducting transitions. The C_P values can provide direct means to verify the BCS character of the superconductivity (energy gap, electron–phonon interaction constant etc.). On the other hand, thermal conductivity being related to charge carriers as well as phonons, gives information about the electron and phonon spectra of the HITSO materials. The PA signal being related to specific heat and thermal conductivity as $I_{PA} \propto C_P^{-1/2} K^{-1/2}$), is also expected to provide similar information for the HITSO materials. Again one has specific heat jump $\Delta C_P = \propto \gamma T_c$ ($\propto$ = constant, and γ is the electronic heat capacity coefficient in the normal states). From BCS theory one finds $C_P/\gamma T_c = 1.43$ (for weak coupling BCS model). Therefore, one might get adequate information about the electron-phonon interaction constant form the PA signal as in the case of specific heat.

A low temperature PA cell used for the studies of HITSO materials in our laboratory is shown in Figure 2.

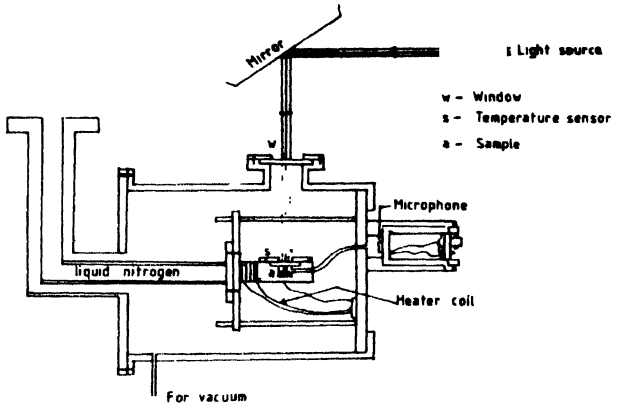

Figure 2. Schematic diagram of the low temperature photoacoustic cell (constructed in our laboratory).

4.1 Preparation of HITSO materials :

There are, in general, three independent routes for the preparation of the HITSO materials in bulk. These are (i) ceramic route where the individual oxide materials like Y_2O_3, CuO, $BaCO_3$ etc. are mixed together and sintered at higher temperatures and slowly cooled to room temperature [13–18], (ii) glass-ceramic route where the individual oxides are mixed together and melted in a platinum or alumina crucible and the melt is quickly quenched to make the glass. This glass is a semiconductor and by properly annealing them to higher temperatures one gets HITSO [19-22] and (iii) the slo-gel and chemical route where the nitrate solutions of the individual metal ions (Y, Ba, Ca, etc.) are made into gels by different processes [23-25]. These gels are dried and properly sintered to get the HITSCO materials. There are also some other methods for the preparations of HITSO which ultimately belong to any of the above three processes. The general behaviour of the thermal

variations of electrical resistance (R) and magentic susceptibilities (χ_{ac} and χ_{dc}) characterizing these materials are shown in Figures 3–5.

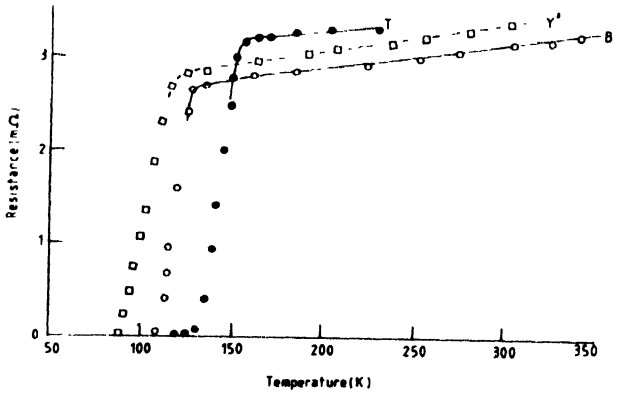

Figure 3. Thermal variations of electrical resistances of the typical Y–Ba–Cu–O (Y), Bi–Sr–Ca–Cu–O (Bi) and Tl–Ba–Ca–Cu–O (Tl) superconductors.

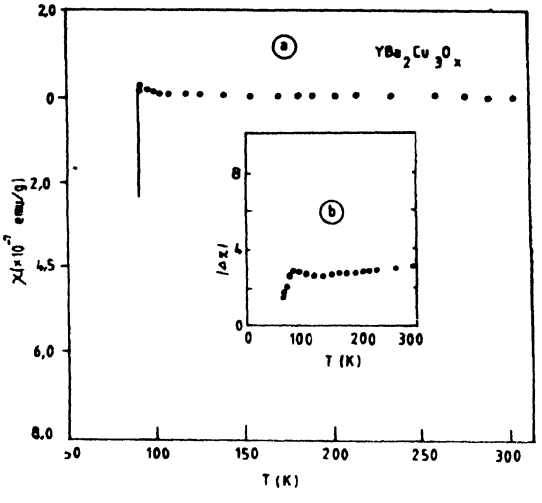

Figure 4. (a) Thermal variation of dc magnetic susceptibility of a Y–Ba–Cu–O superconductors. (b) Data shown from Suzuki *et al* [49].

4.2. The PA spectra of HITSO materials :

The amplitude and phase of the PA signal carry information about the phase transitions and hence superconducting behaviour of the HITSO or other materials.

The basic arrangement of a PA spectrometer is shown in Figure 1 as discussed earlier. The photoacoustic cell, the main part of the instrument, which could be used for a wide range of temperature (400–77K) is shown in Figure 2. In the PA cell configuration the principle of an acoustic Helmtollz resonator [26,27] was used. This configuration permits large variations in the sample temperature without altering the microphone temperature

appreciably. The microphone housing is sealed with a rubber 'O' ring to have good acoustic isolation from the rest of the cryostat assembly.

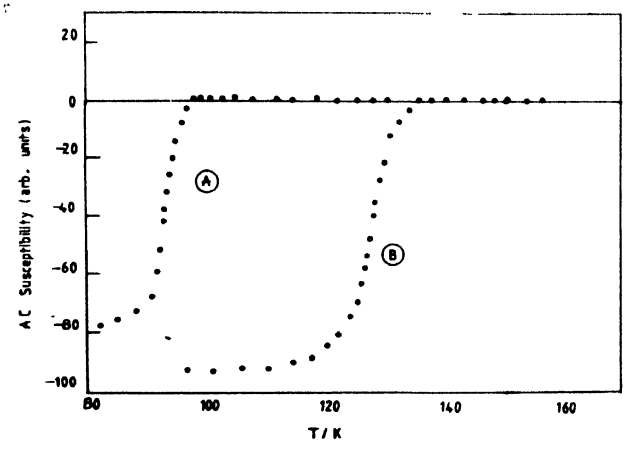

Figure 5. Thermal variations of ac magnetic susceptibilities of some high temperature superconducting oxides.

The sample temperature is detected by resistance thermometer using a temperature controller. The PA signal and the thermo-emf is fed to the computer for analysis and graphical representation (for details see Rosencwaig [5] and Hess [28]).

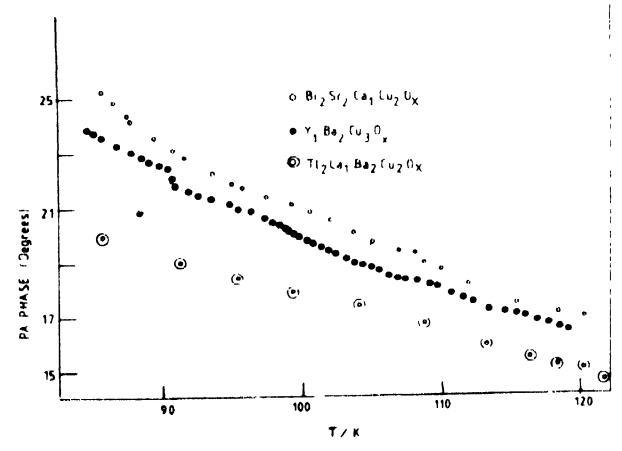

Figure 6. Thermal variations of PA 'phase' changes of some high temperature superconducting oxides.

Figure 6 shows the thermal variation of the PA 'phase' changes for the superconducitng $Y_1Ba_2Cu_3O_x$, $Bi_4Sr_3Ca_3Cu_4O_x$, $Tl_2Ba_2Ca_2Cu_2O_x$ [21, 29–32] samples taken in the forms of thin pellets. The variation of phase with temperature is almost linear. The corresponding variations of the PA amplitude for the superconducting $Y_1Ba_2Cu_3O_x$ and Bi–Sr–Ca–Cu–O systems are shown in Figure 7. A clear anomaly at the superconducting transition temperature is observed for both the systems. Song *et al* [32] also noticed

anomaly in the PA phase variations with temperature at the superconducting transition temperature in Y–Ba–Cu–O system. It is well known that the specific heat anomalies associated with HITSO materials (at T_c) are very small [33, 34] and almost undetectable for the Bi–Sr–Ca–Cu–O systems. Therefore, it is obvious that the PA signal would also indicate very small anomaly around the corresponding superconducting transitions.

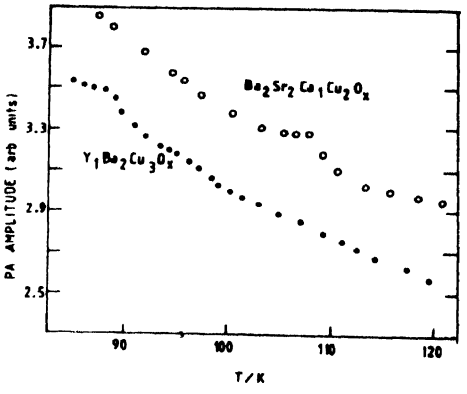

Figure 7. Thermal variations of PA amplitudes of some high temperature superconducting oxides.

According to (R–G) theory, for the optically opaque and thermally thick HITSO samples, the optical absorption length $L_B \ll \mu$ (thermal diffusion length) and the amplitude I_{PA} of the PA signal varies as

$$I_{PA} \propto C_P^{-1/2} K^{-1/2}. \qquad (15)$$

Thermal conductivity [35-37] of Y–Ba–Cu–O sample showed an increase below T_c while specific heat [33, 38], decreases with temperature. This oposite thermal variations of (K) and (C_P) actually reduces the overall effect on the PA amplitude. Optical absorption in $Y_1Ba_2Cu_3O_x$ is concerned mainly in the green region of the spectrum.This also reduces the intensity of the PA signal in the (HITSO) system. For a sample with $L > \mu$ one has

$$I_{PA} \propto C_P^{-1}. \qquad (16)$$

This expression is independent of thermal conductivity. Therefore for $L_\beta \sim \mu$, the effect of thermal conductivity on the amplitude of PA signal will be reduced.

For the (HITSO) materials the intensity of the monochromatic light obtained from 1000W Xenon lamp, for example, with monochromator is not strong enough for detecting the PA signal. It is also difficult to explain the anomalous change observed in the photoacoustic phase during superconducting transition with R–G theory. The decrease in phase may be due to a decrease in the excited electron relaxation times when the materials undergo superconducting transition. A faster relaxation of the optically excited levels leads to a decrease in the PA phase. The faster relaxation might be due to the creation of additional electron traps when the material changes phase. Further explanation might be important for the analysis of the anomalous changes of PA phase in HITSO materials.

Figure 8 shows the change of PA signal as a function of chopping frequency (f) at various temperatures for the Y–Ba–Ca–O system. The general behaviour of (f) versus PA signal curves for the other Bi–Sr–Ca–Cu–O, and Tl–Ba–Ca–Cu–O superconductors are the same as shown in Figure 8. The frequency at which the slope of the curves changes is the characteristic frequency (f_c) from which thermal diffusivity α can be determined using the relation

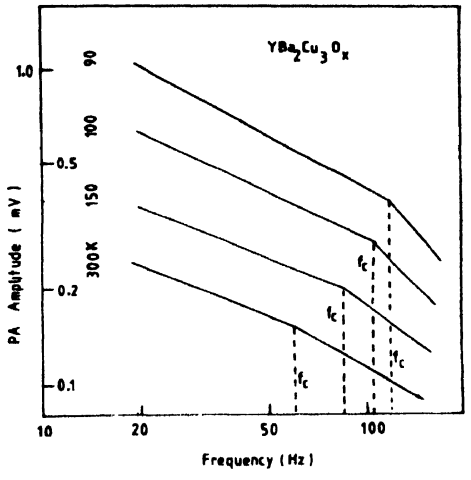

Figure 8. Variation of PA signal with chopping frequency showing a change of slope at a critical frequency (f_c) —a characteristic of the sample.

$$\alpha = f_c L^2 \tag{17}$$

The thermal variation of α for the superconducting samples are shown in Figure 9. There is a sharp increase in thermal diffusivity below the superconducting transition temperature T_c as observed from this figure.

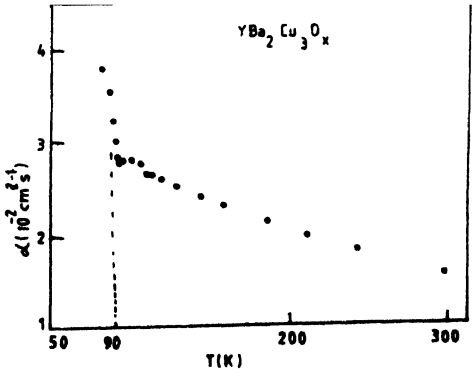

Figure 9. Variation of thermal diffusivity of Y–Ba–Cu–O superconductor with temperature.

In the HITSO phase the electrons from Cooper pairs which cannot carry entropy and so do not contribute to thermal conductivity. Below T_c the number of unpaired electrons

decreases exponentially. Therefore, the thermal conductivity of HITSO falls rapidly below T_c. Again the paired electrons cannot scatter phonons thereby increasing phonon mean free path below T_c. This might increase the phononic contribution to thermal conductivity below T_c. The overall temperature dependence of thermal conductivity below T_c will depend upon which contribution (electronic or phononic) dominates in the superconductor. Thermal diffusivity is related to K and C_p as

$$\alpha = K/\rho C_p \tag{18}$$

(ρ is the density of the sample). Since α depends on the density of the HITSO materials the, PAS might be an important tool for the study of density profile of these materials prepared under different conditions (pressure, temperature, oxygen content etc.). The variation of α with T as shown in Figures 9, 10 might also vary depending on the density of the sample for the same superconductor.

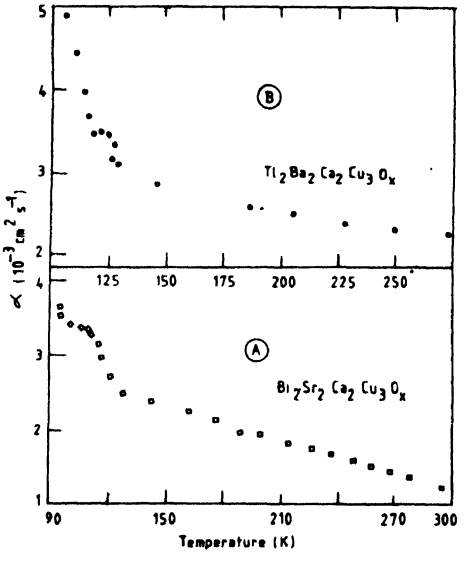

Figure 10. Thermal variations of thermal diffusivities of Tl (B) and Bi (A) bases high temperature oxides.

The phononic contribution to thermal conductivity K_{ph} is given by [39, 40]

$$K_{ph} = 1/3\, C_p \rho V L_P \tag{19}$$

where V and L_P are, respectively, the average sound velocity and the phonon mean free path, therefore

$$\alpha = 1/3\, V L_P. \tag{20}$$

Thus, the increase in the value of α (Figure 9) might also be due to the increase of mean free path L_P caused by the reduction in phonon carier scattering. As the charge carrier begins to form superconducting pairs one can expect this effect. The heat conduction in the HITSO materials is, therefore, mainly due to the phonons. The small decrease of α around T_c (Figure 10) might also be associated with the jump in heat capacity at T_c [33, 38].

The Bi and Tl-based superconductors also behaves almost in a similar manner as shown in Figure 10. The log–log plots of the PA amplitude with chopping frequency of a Bi– and a Tl–based HITSO also show the characteristic change of slope at f_c (critical chopping frequency) as in Figure 8 from which thermal diffusivity α is calculated using (eq.17) and is shown in Figure 10. The change of thermal diffusivity α for different Cu-concentration in the $Bi_4Sr_3Ca_3Cu_yO_x$ (y = 2 to 5) oxides are shown in Figure 11.

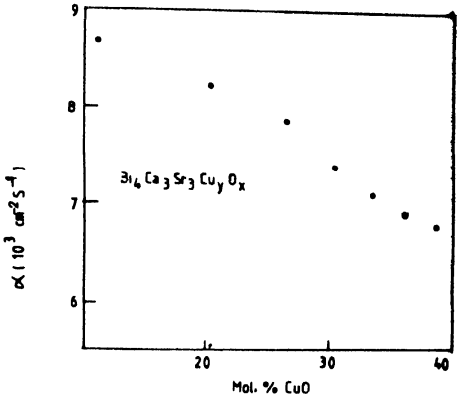

Figure 11. The change of thermal diffusivity with Cu concentration in $Bi_4Ca_3Sr_3Cu_4O_x$ superconductor.

Isaac [29] studied the Pb concentration dependences of thermal diffusivity below T_c in Pb-Bi–Sr–Ca–Cu–O system (Figure 12). He finds that the thermal diffusivity tends to staturate below a critical concentration $x = 0.3$ in $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O$. The increase of Pb concentration might increase the phonon defect scattering resulting in a reduction in phonon mean free path and the corresponding decrease in thermal diffusivity which is evident from Figures 12, 13 below T_c where free electron contribution is absent. For $x > 0.3$ the transport due to free electrons is considerably less in the superconducting phase.

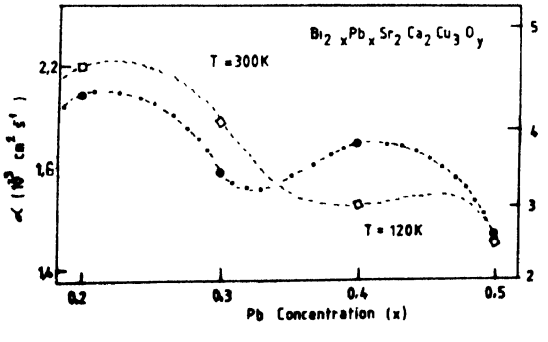

Figure 12. Variation of thermal diffusivity of Pb–Bi–Sr–Ca–Cu–O based superconductors with Pb concentrations (at two fixed temperatures above T_c). Bi–Pb–Ca–Sr–Cu–O based superconductors with Pb concentrations at two different fixed temperatures.

The rise of thermal diffusivity just above T_c (Figures 9, 10) in the $YBa_2Cu_3O_x$ (123), for example, is rather very interesting. Similar increase in dc magnetic susceptibilities [19, 20], heat capacity [41] etc. have also been observed in the same sample. This increase might be due to several causes like different oxygen content in the sample, multiphase character, or due to the antiferromagnetic type character which is suppressed due to the appearance of HITSO phase below T_c. Increase of thermal diffusivity

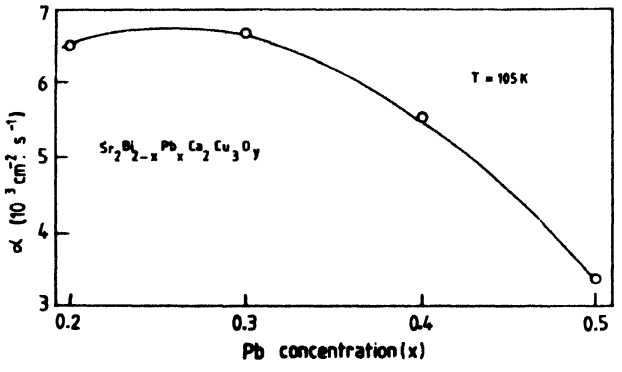

Figure 13. Variations of thermal diffusivity of Bi–Pb–Ca–Sr–Cu–O based superconductors with Pb concentrations at fixed temperature.

just above T_c and then a small decrease and again a small increase with further decrease of temperature is a result of anomalous variation of L_P , the phonon mean free path which in turn is caused by a drastic reduction of phonon carrier scattering. We believe that in the HITSO systems there are several scattering mechanisms like phonon–phonon, electron–phonon, and phonon-spin (since the materials are slightly paramagnetic above T_c). From dc magnetic measurements one also finds a similar small increase of paramagnetic susceptibility (χ) around T_c [21, 42, 43] followed by a drastic change of sign of χ to the superconducting phase at T_c. This small rise in magnetic susceptibility, is considered by us to arise from antiferromagnetic (AFM) interaction mechanism responsible for the appearance of superconductivity in HITSO oxides. The paramagnetic character increases very slightly as the temperature decreases down to around T_c . The superconducting paring interaction becomes strong enough to just suppresses the antiferromagnetic ordering mechamism. The magnetic susceptibility χ above T_c could be expressed as

$$\chi = \chi_0 + C/(T - \theta) \tag{21}$$

where θ is the Curie-temperature varying from –10 to –15K for the Y–Ba–Cu–O. Since just above T_c the AFM character vanishes, one of the scattering process viz. spin-phonon diminshes giving rise to a small rise in α above T_c (Figures 9, 10) and just below this temperature i.e. at $T < T_c$ the main phonon scattering agent is diminished giving rise to a large increase of α below T_c. Because, at this stage most of the phonon carriers are used up to form Cooper pairs. Thus one really expect anomalous variation of α, C_p, χ etc. around

T_c arising due to the common orgin. If this contention is correct the superconducting pairing mechanism in HITSO might be explained by considering superexchange type interaction in the following manner.

From the studies of the magnetic properties of La_2CuO_4 type materials [44] one finds a spin density wave or antiferromagnetic transition near 250K. Similar behaviour is supposed to occur even for the Y based compounds. The spins from the Cu 3*d* electrons are ordered antiferromagnetically by the superexchange interaction (Cu–O–Cu type) and, therefore, one has antiferromagnetic spin wave as low-lying excitation modes. Again the conduction electrons (holes) [42, 45] of the oxygen 2*p* band acquire an attractive interaction by exchanging antiferromagnetic spin waves which give rise to high temperature superconductivity. [This is, however, not related to spin fluctuation theory of Miyake *et al* [46]. The above mechanism will lead to a model Hamiltonian [47] of the form

$$H = -t \sum_{(l,n)} C_{lm}+C_{nm} + 2j \sum_{(l,n)} \left(S_l^x S_n^x + S_l^y S_n^y + A\, S_l^z S_n^z \right) +$$

$$J_{sd} \sum_q C_{qm}+C_{qm'} \left[(s^x)_{mm'} S_q^x + (s^y)_{mm'} S_q^y \right] \qquad (22)$$

where A is the anisotropy parameters, the conduction electrons (holes) and spin $S = 1/2$ interacting *via* 'sd' type interaction on a $2D$ square lattice. Such a model would lead to superconducting transition temperature

$$T_c = 4.56\, A \exp(-A/B) \qquad (23)$$

where $B = J_{sd}^2 / 8tJ$ (when $A \gg 1$). This eq. (23) explains the superconducting transitions in HITSO materials quite satisfactorily.

Another possibility of anomalous variation of thermal diffusivity and magnetic susceptibility as mentioned above, might be due to spin Pierels transitions in the Y–Ba–Cu–O system. This is because of the fact that in layered compounds of copper like Cu–HI and also in CuCl the anomalous behavior arising due to Pierels transitions appears almost similar to that observed in YBaCuO system around T_c (as discussed above). In this connection we should mention that one might find some interesting theoretical approach for anisotropic layered superconductors from the work of Jha [48]. We further like to mention that to separate as well as to find the effect of magnetic interactions, if any, in the HITSO materials we are studying the photoacoustic effect in presence of magnetic field.

However, we must wait a little more to get further support to verify this conjecture from other experimental and theoretical findings.

5. Conclusion

In the present review we have attempted to show the importance of photoacoustic studies of high temperature superconducting materials. From these studies, information about the

thermal diffusivity of these materials, strength of electron–phonon interaction etc. have been obtained. It is further, observed that the electron–phonon and spin–phonon type magnetic interactions are important for understanding the thermal behaviour of the HITSO materials along with their magnetic properties. This conclusion finally led to the development of a theoretical model for calculating the superconducting transition temperature in the HITSO materials with success. From all these considerations it is also finally concluded that the PAS technique might be well applied for the non-destructive characterizations of the highly opaque HITSO materials of current interest elucidating many of their salient features not directly available with any other spectroscopic technique developed so far.

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